$(CO)_4$, 29890-04-8; $((dpp)_2e)Mo(CO)_4$, 15444-66-3; $((dpp)_2e)W(CO)_4$, 29890-05-9; $((dpp)_2m)Cr(CO)_4$, 16743-46-7; $((dpp)_2m)Mo(CO)_4$, 26743-81-7; $((dpp)_2m)W(CO)_4$, 41830-14-2; $((dpp)_2oe)Cr(CO)_4$, 50860-44-1; $((dpp)_2oe)Mo(CO)_4$, 50860-45-2; $((dpp)_2oe)W(CO)_4$, 50860-46-3; $((dpp)op)Cr(CO)_4$, 50860-47-4; $((dpp)op)Mo(CO)_4$, 50860-48-5; $((dpp)op)W(CO)_4$, 50860-49-6; $((dpp)_2oe)PdCl_2$, 50860-50-9; $((dpp)_2op)PdCl_2$, 50860-51-0; $((dpp)_2oe)HgBr_2$, 50860-52-1; $((dpp)_2oe)HgI_2$, 50860-53-2; $(dpp)_2oe$, 50860-54-3; $(dpp)_2op$, 32309-62-9; $(dpp)_2m$, 2071-20-7; $(dpp)_2e$, 1663-45-2; $(dpp)_2p$, 6737-42-4; Ph_2PLi, 15968-89-5; C_2H_4O, 75-21-8; Ph_2PCl, 1079-66-9; Ph_2POCH_3, 4020-99-9; Ph_2PCH_2OH, 5958-44-1; $W(CO)_6$, 14040-11-0; $Cr(CO)_6$, 13007-92-6; $(C_6H_5CN)_2PdCl_2$, 14220-64-5; ^{31}P, 7723-14-0.

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Yellow Springs, Ohio 45387

Preparation and Characterization of Two Series of Dimeric Molybdenum(V) *N,N*-Dialkyldithiocarbamates. Their Interrelationship and Chemistry as a Model for the Active Site of Nitrogenase

W. E. NEWTON,* JAMES L. CORBIN, DUDLEY C. BRAVARD, JOHN E. SEARLES, and JOHN W. McDONALD

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Refluxing aqueous solutions containing molybdenum(V) react with sodium *N,N*-dialkyldithiocarbamates (Na(dtc); 1 mol) to yield a series of new complexes, $Mo_2O_4(dtc)_2$, while at 0° with Na(dtc) (>4 mol), $Mo_2O_3(dtc)_4$ is produced. The former complexes may be converted to the latter by further reaction with Na(dtc). Assignments of the molybdenum–oxygen stretching frequencies in the infrared spectra have been made and the visible spectra have been investigated. The interrelationship and chemistry of these two types of complex are suggested as a possible model for the interaction of two molybdenum atoms at an enzymic active site.

There is at present a growing interest in the chemistry of coordination compounds of molybdenum, particularly because of their possible relationship to redox-active molybdoenzymes.[1] The most recent reports suggest that the iron-molybdenum protein component[2] of nitrogenase (component I) (from *Azotobacter vinelandii*[2] or *Clostridium pasteurianum*,[3] but not from *Klebsiella pneumoniae*[4]) and xanthine oxidase (from all known sources[5]) both contain two molybdenum atoms per mole of enzyme. There is a distinct possibility in these cases that the two molybdenum atoms are at the active site, working in conjunction during catalysis. As part of our studies[6] of models for such enzymes, we sought to investigate this possibility and chose the supposedly well-established dimeric molybdenum(V) dithiocarbamates, *i.e.*, $Mo_2O_3(dtc)_4$, as our initial subject. This choice was dictated primarily by our recent successful reduction of diethyl azodicarboxylate (a useful two-electron acceptor model) by some *N,N*-dialkyldithiocarbamate complexes of molybdenum(IV). This reduction was accomplished by an initial oxidative addition of the azo double bond thus forming a 1:1 adduct, followed by hydrolysis to give the substituted hydrazine and the appropriate *cis*-dioxomolybdenum(VI) complex.[6] One to one adducts were also prepared with some related acetylenic and olefinic compounds.[6]

In this paper, we describe the synthesis and characterization of a new type of molybdenum(V) dithiocarbamate complex, μ-dioxo-bis[oxo-*N,N*-dialkyldithiocarbamatomolybdenum(V)], $Mo_2O_4(dtc)_2$, and an improved method for the preparation of μ-oxo-bis[oxobis(*N,N*-dialkyldithiocarbamato)molybdenum(V)], $Mo_2O_3(dtc)_4$. Assignments of the various molybdenum–oxygen vibrations in the infrared spectra have been made and the visible spectra have been reinvestigated and interpreted. The interrelationship of these two types of complex and some of their relevant chemistry are described and used as a basis for a possible mechanism of interaction for two molybdenum atoms at enzymic active sites.

Experimental Section

Materials and Physical Measurements. The known sodium salts of the dithiocarbamic acids were prepared in the customary manner[7] by dropwise addition of the appropriate dialkylamine (1.0 mol) to carbon disulfide (1.1 mol) in aqueous ethanol at room temperature, followed by dropwise addition of 10 *N* sodium hydroxide (1.0 mol). After the mixture had stood for several hours, the salt could usually be crystallized by the addition of acetone and then chilling to 0°. In the case of the diisopropyl compound a reaction temperature of 40° was used and the solvent was ether–acetone. All gave satisfactory C, H, and N analyses which indicated varying degrees of hydration.

All reactions and physical measurements were carried out under an atmosphere of purified argon using degassed analytical reagent grade solvents.

Infrared spectra were recorded as KBr disks with a Beckman IR-20A spectrophotometer, visible spectra were measured with a Cary Model 14 recording spectrophotometer, and microanalyses were obtained with a Hewlett-Packard 185 CHN Analyzer.

All analytical data are collected in Table I.

Preparation of $Mo_2O_3(dtc)_4$ Complexes. A solution of molybdenum pentachloride (0.50 g, 1.8 mmol) in water (50 ml) was slowly added to an ice-cold solution of the dithiocarbamate salt (*ca.* 18 mmol) in water (50 ml). The dark purple precipitate of $Mo_2O_3(dtc)_4$ (*ca.* 70% yield), which formed immediately, was collected by filtration, washed thoroughly with water, and dried *in vacuo*.

Preparation of $Mo_2O_4(dtc)_2$ Complexes. In a typical preparation, a solution containing molybdenum pentachloride (2.0 g, 7.3 mmol) and the dithiocarbamate salt (7.3 mmol) in water (50 ml) was

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[1] See, *e.g.*, J. T. Spence, *Coord. Chem. Rev.*, 4, 475 (1969).

[2] W. A. Bulen and J. R. LeComte, *Proc. Nat. Acad. Sci. U. S.*, 56, 979 (1966); W. A. Bulen and J. R. LeComte, *Methods Enzymol.*, 24, 470 (1972); and unpublished data that show two molybdenum atoms per molecular weight of *ca.* 230,000.

[3] W. G. Zumft, W. C. Cretney, T. C. Huang, L. E. Mortenson, and G. Palmer, *Biochem. Biophys. Res. Commun.*, 48, 1525 (1972).

[4] R. R. Eady, B. E. Smith, K. A. Cook, and J. R. Postgate, *Biochem. J.*, 128, 655 (1972); a subsequent personal communication from these authors indicates that more than one molybdenum atom per mole may be present.

[5] R. C. Bray, P. F. Knowles, and L. S. Meriwether in *Magn. Resonance Biol. Syst., Proc. Int. Conf., 1966*, 221 (1967).

[6] W. E. Newton, J. L. Corbin, P. W. Schneider, and W. A. Bulen, *J. Amer. Chem. Soc.*, 93, 268 (1971); P. W. Schneider, D. C. Bravard, J. W. McDonald, and W. E. Newton, *ibid.*, 94, 8640 (1972); J. W. McDonald, J. L. Corbin and W. E. Newton, unpublished data.

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refluxed until the initial purple precipitate changed to yellow (*ca.* 0.5-2 hr depending on the ligand used). The $Mo_2O_4(dtc)_2$ product (*ca.* 55% yield) was isolated by filtration, washed with water, ethanol, and diethyl ether, and dried *in vacuo*.

Conversion of $Mo_2O_4(dtc)_2$ to $Mo_2O_3(dtc)_4$. Typically, $Mo_2O_4(dtc)_2$ (0.3-0.5 g, 0.5 mmol) and the sodium salt of the appropriate ligand (1.0 mmol) were stirred in a 1:1 mixture of chloroform-methanol (*ca.* 40 ml) for *ca.* 18 hr. The purple precipitate of $Mo_2O_3(dtc)_4$ (confirmed by infrared spectrum and analysis; *ca.* 60% yield) was collected by filtration, washed with methanol and diethyl ether, and dried *in vacuo*.

Reaction of μ-Oxo-bis[oxobis(*N,N*-dialkyldithiocarbamato)molybdenum(V)] with Diethyl Azodicarboxylate. (a) μ-Oxo-bis[oxobis(*N,N*-dimethyldithiocarbamato)molybdenum(V)]. To a stirred suspension of $Mo_2O_3(S_2CNMe_2)_4$ (0.21 g, 0.20 mmol) in dichloromethane (75 ml) diethyl azodicarboxylate (0.12 g, 0.60 mmol) was added. The purple color was discharged and all the solid dissolved during 1 hr to give a yellow solution, which was then evaporated to dryness. The oily yellow solid was extracted with dry hexane (three 25-ml portions) to remove excess diethyl azodicarboxylate and then dried *in vacuo*. The infrared spectrum of this solid corresponded to a mixture of $MoO_2(S_2CNMe_2)_2$ (ν(Mo=O) at 910 and 873 cm^{-1}) and the 1:1 adduct[6] $MoO(S_2CNMe_2)_2(EtO_2CN{=}NCO_2Et)$ (ν(Mo=O) at 933 cm^{-1}, ν(C=O) at 1710 and 1725 cm^{-1}). Extraction with dry benzene (two 10-ml portions) gave a yellow residue of *cis*-dioxobis(*N,N*-dimethyldithiocarbamato)molybdenum(VI) (0.10 g, 91% yield) (identified by infrared spectrum). Evaporation of the benzene extract gave the 1:1 diethyl azodicarboxylate-oxobis(*N,N*-dimethyldithiocarbamato)molybdenum(IV) adduct (0.11 g, 75%) (identified by infrared spectrum).

(b) μ-Oxo-bis[oxobis(*N,N*-diethyldithiocarbamato)molybdenum(V)]. In a similar experiment, after evaporation of the reaction mixture to dryness and extraction with hexane, a yellow residue of *cis*-dioxobis(*N,N*-diethyldithiocarbamato)molybdenum(VI) and the 1:1 diethyl azodicarboxylate-oxobis(*N,N*-diethyldithiocarbamato)molybdenum(IV) adduct (identified by infrared spectrum) was obtained. In the several experiments attempted, some variable contamination with 1,2-bis(ethoxycarbonyl)hydrazine (ν(NH) at 3270 cm^{-1} and ν(C=O) at 1770 and 1715 cm^{-1}) was observed.

(c) μ-Oxo-bis[oxobis(1-piperidinecarbodithioato)molybdenum(V)] and μ-Oxo-bis[oxobis(4-morpholinecarbodithioato)molybdenum(V)]. In both cases, evaporation to dryness followed by hexane extraction gave a mixture of the appropriate *cis*-dioxomolybdenum(VI) compound and 1:1 diethyl azodicarboxylate-molybdenum(IV) adduct (identified by infrared spectrum). No substituted hydrazine was observed in either system.

Table I. Analytical Data

Compd	% calcd C	% calcd H	% calcd N	% found C	% found H	% found N
$Mo_2O_3(S_2CNMe_2)_4$	20.0	3.3	7.8	19.4	3.5	7.5
$Mo_2O_4(S_2CNMe_2)_2$	14.5	2.4	5.7	14.5	2.5	5.5
$Mo_2O_3(S_2CNEt_2)_4$	28.8	4.8	6.7	28.5	4.8	6.6
$Mo_2O_4(S_2CNEt_2)_2$	21.7	3.6	5.1	21.8	3.8	4.9
$Mo_2O_3[S_2C(1\text{-pip})]_4$	32.7	4.6	6.4	33.8	4.9	6.1
$Mo_2O_4[S_2C(1\text{-pip})]_2$	25.0	3.5	4.9	24.4	3.3	4.6
$Mo_2O_3[S_2C(4\text{-morph})]_4$	27.0	3.6	6.3	27.1	3.8	6.3
$Mo_2O_4[S_2C(4\text{-morph})]_2$	21.9	2.9	5.1	20.5	2.8	4.7
$Mo_2O_3(S_2CN(i\text{-Pr})_2)_4$	35.6	5.9	5.9	35.5	5.9	5.9

Results

Preparation and Characterization of Compounds. None of the previously reported preparative methods[8-12] for these dimeric molybdenum(V) dithiocarbamates were wholly satisfactory. Initial experiments using acidification,[8,12] by sulfur dioxide or 10 *M* hydrochloric acid, of aqueous solutions of sodium molybdate (1 mol) and sodium *N,N*-dialkyldithiocarbamate (Na(dtc); 4 mol) led to mixtures[13] of *cis*-dioxobis(*N,N*-dialkyldithiocarbamato)molybdenum(VI) [*cis*-$MoO_2(dtc)_2$] and $Mo_2O_3(dtc)_4$ (by infrared spectroscopy). Similar reaction mixtures, heated near their boiling point and acidified with 10 *M* hydrochloric acid, gave dark purple precipitates[8,12] whose analyses were close to those of the compounds $Mo_2O_3(dtc)_4$ and contained no bands due to *cis*-$MoO_2(dtc)_2$ in their infrared spectra. These products were virtually insoluble in common organic solvents. In contrast, the $Mo_2O_3(dtc)_4$ complexes produced by us at or below ambient temperature have appreciable solubility. This heating technique appears, therefore, to enhance the intermolecular reactions which have been suggested[8,10] to occur for the $Mo_2O_3(dtc)_4$ complexes and so produces oligimers rather than the desired dimer. The anaerobic sodium dithionite reduction[10,11] of aqueous 1:2 molybdate-dithiocarbamate mixtures gave pink molybdenum(IV) products.[6,14] Only in the presence of air did purple, and therefore molybdenum(V), products predominate from the dithionite reduction. This latter technique, however, is unsatisfactory because the competing reactions of oxidation of molybdenum(V) by oxygen and its reduction by sodium dithionite to molybdenum(IV), as well as the reaction of oxygen with sodium dithionite, allow minimal control both during the reaction and in the work-up of products. A similar objection applies to the method[9] using molecular oxygen to prepare these complexes from $Mo(CO)_2(S_2CNEt_2)_2$.

To overcome these difficulties, reaction 1 was attempted.[10]

$$2(NH_4)_2MoOCl_5 + 4Na(dtc) \rightarrow Mo_2O_3(dtc)_4 \qquad (1)$$

No pure $Mo_2O_3(dtc)_4$ was isolated from the several experiments performed. The presence of a second molybdenum species, possibly $Mo_2O_4(dtc)_2$, was suggested by infrared bands at ~980 cm^{-1} (ν(Mo=O)) and ~740 cm^{-1} (νMoO_2Mo)). These bands had been observed previously[15-21] with amino acid complexes of molybdenum(V) of the type $Mo_2O_4L_2$ (L = anionic, bi- or tridentate ligand) and their formation was accelerated by heating the reaction mixtures.[15] Therefore, an equimolar aqueous solution of sodium *N,N*-dialkyldithiocarbamate and the anaerobic hydrolysis product of molybdenum pentachloride ("molybdenum(V) oxochloride") was refluxed in argon until the initial purple precipitate changed to yellow (*ca.* 0.5-2 hr depending on the ligand used). Analytical (Table I) and infrared (Table II) data were consistent with the formulation $Mo_2O_4(dtc)_2$ [dtc = RCS_2^-; R = $(CH_3)_2N$, $(C_2H_5)_2N$, 4-morpholine, 1-piperidine, but not $[(CH_3)_2CH]_2N$ (when a mixture with $Mo_2O_3(dtc)_4$ was obtained)] for these yellow precipitates. Alternatively, when aqueous "molybdenum(V) oxochloride" was added slowly to an ice-cold aqueous solution of Na(dtc) (>4 mol), dark purple, analytically pure $Mo_2O_3(dtc)_4$ [dtc = RCS_2^-; R = $(CH_3)_2N$, $(C_2H_5)_2N$, $[(CH_3)_2CH]_2N$, 4-morpholine, 1-piperidine] was precipitated (see Table I for analytical data and Table II for infrared data). In the *N,N*-dimethyl- and *N,N*-diethyldithiocarbamate systems, $Mo_2O_4(dtc)_2$ could be easily converted to $Mo_2O_3(dtc)_4$ by stirring with the ap-

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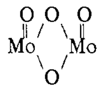
Table II. Selected Infrared Spectral Data (cm^{-1})

Compd	ν(Mo=O)	ν(MoO$_2$Mo)	ν(MoOMo)	ν(MoS)
$Mo_2O_3(S_2CNMe_2)_4$	938 s		435 m, 758 w	370 m
$Mo_2O_4(S_2CNMe_2)_2$	960 m, 978 s	480 m, 736 m		388 m
$Mo_2O_3(S_2CNEt_2)_4$	938 s		438 m, 750 w	370 m
$Mo_2O_4(S_2CNEt_2)_2$	960 m, 977 s	480 m, 733 m		382 m
$Mo_2O_3[S_2C(1\text{-pip})]_4$	938 s		440 m, 750 w	360 m
$Mo_2O_4[S_2C(1\text{-pip})]_2$	965 m, 980 s	472 m, 732 m		365 m
$Mo_2O_3[S_2C(4\text{-morph})]_4$	940 s		435 m, 735 w	365 m
$Mo_2O_4[S_2C(4\text{-morph})]_2$	965 m, 982 s	470 w, 734 m		360 m
$Mo_2O_3(S_2CN(i\text{-Pr})_2)_4$	943 s		438 m, 758 w	400 m

propriate ligand in 1:1 chloroform–methanol solution. Only partial conversion occurred for the morpholino- and piperidinodithiocarbamate systems.

Infrared Spectra. The infrared spectra of $Mo_2O_4L_2$ complexes contain four bands assignable to the



moiety. A strong band at ~980 cm^{-1} and a weaker band at ~970 cm^{-1} are due to the terminal Mo=O vibrations. The symmetric and antisymmetric bridge vibrations for the complexes occur at ~480 and ~740 cm^{-1}, respectively. These assignments are consistent with those made for amino acid and related complexes of Mo(V).[15-23]

The assignments made in the infrared spectra of Mo_2O_3(dtc)$_4$ complexes are terminal Mo=O at ~940 cm^{-1} and the symmetric and antisymmetric bridge vibrations at ~430 and ~750 cm^{-1}, respectively. Table II contains selected infrared data for both types of complex.

Visible Spectra. The visible spectra of all Mo_2O_4(dtc)$_2$ complexes were essentially featureless except for a poorly resolved shoulder at ~370 nm. The spectra of the Mo_2O_3(dtc)$_4$ compounds, however, contained an intense band at ~510 nm and a shoulder at ~380 nm. The previously reported[11] band at ~620 nm (ε 2900) was not observed in any of our spectra. Visible spectral data for the Mo_2O_3(dtc)$_4$ compounds, together with data for the appropriate molybdenum(VI) [MoO_2(dtc)$_2$] and molybdenum(IV) [MoO(dtc)$_2$] complexes,[6] are listed in Table III. The band at ~510 nm did *not* obey Beer's law and its molar absorptivity decreased markedly as the concentration was lowered. An independent observation of this phenomenon has been reported recently.[24] In contrast, we have found that the band at ~380 nm obeys Beer's law. Molar absorptivities as a function of concentration in benzene solution are shown for Mo_2O_3(dtc)$_4$ in Table IV. This deviation from Beer's law by the 510-nm band accounts for the discrepancies in molar absorptivity in previous reports of the visible spectrum[10,11] of $Mo_2O_3(S_2CNEt_2)_4$. The deviation was shown to be reversible by diluting a solution of the 1-piperidinecarbodithioatomolybdenum(V) dimer twofold and then reconcentrating it by evaporation when both the original and final solutions had the same molar absorptivity at 510 nm. This behavior is therefore due to an equilibrium rather than a decomposition reaction and may be rationalized by the dissociation of the molybdenum(V) dimer into molybdenum(VI) and molybdenum(IV) monomers: $Mo_2O_3(dtc)_4 \rightleftharpoons MoO_2(dtc)_2 + MoO(dtc)_2$.

Table III. Visible Spectral Data for Various Molybdenum Dithiocarbamates[a]

$Mo_2O_3(S_2CNEt_2)_4$[b]	513 (?)[c]	378 (5200)
$MoO_2(S_2CNEt_2)_2$[b,d]		374 (3430)
$MoO(S_2CNEt_2)_2$[b,d]	508 (670)	385 (1730)
$Mo_2O_3[S_2C(1\text{-pip})]_4$[b]	512 (?)[c]	378 (5880)
$MoO_2[S_2C(1\text{-pip})]_2$[b,d]		374 (4170)
$MoO[S_2C(1\text{-pip})]_2$[b,d]	502 (715)	386 (1950)
$Mo_2O_3[S_2C(4\text{-morph})]_4$	515 (?)[b,c]	372 (5640)
	512 (?)[c,e]	377 (5500)
$MoO_2[S_2C(4\text{-morph})]_2$[d]		372 (4255)[b]
		375 (3680)[e]
$MoO[S_2C(4\text{-morph})]_2$[d,e]	508 (715)	388 (1600)

[a] Peak maxima in nm; molar absorptivities in parentheses. [b] In benzene solution. [c] See Table IV for molar absorptivity data. [d] Preparation and properties to be reported. [e] In chloroform solution.

Table IV. Molar Absorptivities for Mo_2O_3(dtc)$_4$ as a Function of Concentration in Benzene Solution[a]

Complex	Concn	ε ~510	ε ~380
$Mo_2O_3(S_2CNEt_2)_4$	2.57	3.74	5.21
	1.29	2.33	5.20
	0.86	1.86	5.11
	2.57[b]	3.65	5.20
$Mo_2O_3[S_2C(1\text{-pip})]_4$	2.73	3.54	5.88
	1.36	2.32	5.88
	0.68	1.59	5.88
	2.73[b]	3.39	5.86
$Mo_2O_3[S_2C(4\text{-morph})]_4$	1.24	4.92	5.80
	0.62	3.38	5.48
	1.24[b]	4.80	5.78

[a] Exact position of peak maxima are set out in Table III; concentration in $M \times 10^4$; molar absorptivity $\times 10^{-3}$. [b] Spectrum of original concentration was rerun after standing under argon for 30 min to eliminate the possibility of solvolysis causing the decrease in ε.

The species produced by this dissociation were determined by three methods. First, on mixing equimolar solutions of the appropriate concentration of the various molybdenum(IV) and molybdenum(VI) complexes spectra identical with those of solutions made directly from the molybdenum(V) dimer were produced. Second, from our previous work[6] of preparing adducts of the molybdenum(IV) species with diethyl azodicarboxylate and related molecules, we were able to trap the molybdenum(IV) as its 1:1 diethyl azodicarboxylate adduct and so force the equilibrium completely to the right. Mixtures of the 1:1 adduct and the *cis*-dioxomolybdenum(VI) complex were obtained in these experiments. The *N,N*-dimethyldithiocarbamatomolybdenum(V) dimer was chosen for an experiment in which complete product separation was attempted because the *cis*-dioxomolybdenum(VI) complex of this ligand is the least soluble in organic solvents and the oxobis(*N,N*-dimethyldithiocarbamato)molybdenum(IV)-diethyl azodicarboxylate adduct is the least susceptible to hydrolysis of all the adducts we prepared.[6] This last experiment showed that approximately equimolar quantities of the 1:1 adduct and *cis*-dioxomolybdenum(VI) complex were formed and so confirmed the equilibrium. Third, conductance measurements on solutions of the various Mo_2O_3(dtc)$_4$ complexes indicated that no ions were formed.

Discussion

The complex $Mo_2O_3(S_2CNEt_2)_4$ has been the subject of

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several investigations[9-12] since it was originally prepared[8] and discrepancies in both the description of its physical properties and spectral studies have appeared in the literature. Our studies[6] of complexes of molybdenum containing sulfur donor ligands as possible models for the active site of certain enzymes has led to a reinvestigation of this compound and several closely related ones.

Initial attempts by previously described methods to synthesize the compounds $Mo_2O_3(dtc)_4$ (dtc = RCS_2; R = Me_2N, Et_2N, *i*-Pr_2N, 1-piperidine, 4-morpholine) led to unsatisfactory products for reasons previously stated. The discovery of the $Mo_2O_4(dtc)_2$ complexes in the aqueous reaction mixtures produced from "molybdenun(V) oxochloride" or ammonium oxopentachloromolybdate(V) with the various ligands probably explains the previous inability[10] to prepare an analytically pure sample of $Mo_2O_3(S_2CNMe_2)_4$. The use of a large excess of ligand and low temperature, however, does give pure $Mo_2O_3(dtc)_4$ complexes. No pure $Mo_2O_4(dtc)_2$ product could be isolated from reaction mixtures by using sodium *N,N*-diisopropyldithiocarbamate. The product retained its purple color even after 2 days of refluxing but did have a ~740-cm^{-1} band in its infrared spectrum and is probably a mixture containing both types of complex.

No X-ray structural data are available for the compounds $Mo_2O_3(dtc)_4$, but due to their similar spectroscopic properties (see below), they are likely to have structures similar to the analogous xanthate[25] (I) and dithiophosphate[26] (II) compounds. Similarly, the compounds $Mo_2O_4(dtc)_2$ are suggested to have structures closely related to the molybdenum(V) complex[22] with L-cysteine ethyl ester (III).

Infrared Spectra. There has been much disagreement[9-12] about the assignments in the infrared spectrum of $Mo_2O_3(S_2CNEt_2)_4$, particularly concerning the various molybdenum-oxygen stretching frequencies. The two series of complexes prepared in this work, together with the data obtained for the analogous molybdenum(IV) and molybdenum(VI) complexes,[6] presented an opportunity to make more definite assignments.

We assign the strong band at ~940 cm^{-1}, which is unique to the spectra of the purple $Mo_2O_3(dtc)_4$ compounds, to the terminal molybdenum-oxygen stretching vibration [ν(Mo=O)]. The weak to medium absorptions at ~750 and ~430 cm^{-1}, which appear only in the purple compounds, are attributed to the antisymmetric and symmetric vibrations of the Mo-O-Mo bridge. Our independently derived data and assignments agree with those recently published[12] for $Mo_2O_3(S_2CNEt_2)_4$, except for the assignment in that work of a weak shoulder at ~910 cm^{-1} to a second ν(Mo=O). We suggest that this absorption may be due to a dithiocarbamate ligand vibration. The bands at ~1000 cm^{-1} previously assigned to ν(Mo=O) in the *N,N*-diethyldithiocarbamate[11] and analogous ethyl xanthate[11,27] complexes are suggested to be due to C-S absorption of the ligand.

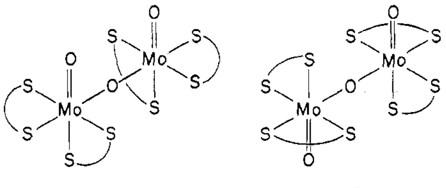

(I) $Mo_2O_3(S_2COEt)_4$ (II) $Mo_2O_3[S_2P(OEt)_2]_4$

Figure 1.

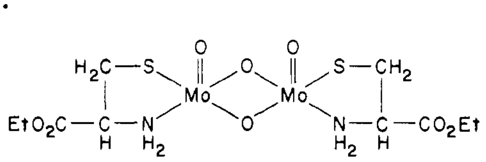
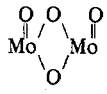

(III) $Mo_2O_4[SCH_2CH(NH_2)CO_2Et]_2$

Figure 2.

In the series $Mo_2O_4(dtc)_2$, ν(Mo=O) is shifted to higher frequency and is definitely split into two absorptions. The higher of these two absorptions (~980 cm^{-1}) is much stronger than the second band (~970 cm^{-1}). The Mo-O_2-Mo bridge vibrations are thought to be the medium absorptions at ~740 cm^{-1} (antisymmetic) and ~480 cm^{-1} (symmetric). These correlations are consistent with those made in other complexes suggested to have the MoO_2Mo bridge.[15-17,23] In fact, the split band at ~980 cm^{-1} and the medium, very sharp absorption at ~740 cm^{-1} appear in all the complexes we[6] and others have prepared with many different ligands and they can be used as good indicators of the presence of the



moiety in complexes. These bridge assignments are supported by the absence of these bands in the products of reaction of $Mo_2O_4(dtc)_2$ with hydrogen sulfide in chloroform solution (where the bridging sulfides only are replaced).[6] In both series of compounds, a medium absorption at ~360-380 cm^{-1} is attributed to molybdenum-sulfur stretching.

Visible Spectra. The data obtained from the visible spectral study of the $Mo_2O_3(dtc)_4$ complexes, which links the non Beer's law behavior of the 510-nm band with an equilibrium involving dissociation of the molybdenum(V) dimer into molybdenum(IV) and molybdenum(VI) monomers, suggests that the ~510-nm band is due to a transition involving the Mo-O-Mo bridge. The intepretation previously proposed[25] to explain the origin of a similar band in the electronic spectrum of the analogous ethyl xanthate complex is therefore likely to be applicable to the dithiocarbamate dimers.

Rather surprisingly, the 380-nm band in these spectra obeyed Beer's law throughout the concentration range studied (see Table IV). This observation suggests either that the molar absorptivities at this wavelength of the three species present in solution have the same value or that the sum of the molar absorptivities for the molybdenum(IV) and molybdenum(VI) species equals that for the molybdenum(V) dimer. Scrutiny of Table V shows that the former reason is incorrect but that the latter satisfies this observation. Further (see Table V), it is seen that the value of the molar absorptivity at 380 nm appears to be a direct function of the number of oxo ligands per molybdenum. It may therefore be deduced that this absorption is due to a molybdenum-oxygen transition and that the molar absorptivity at 380 nm for an oxomolybdenum moiety in these dithiocarbamate systems is *ca.* 1800. The systematic variation found in ϵ makes it unlikely that the 380-nm absorption is concerned with the dithiocarbamate ligands as all three species have two bidentate ligands present per molybdenum.

Relevance to Molybdenum in Enzymes. Although there have been many recent reports of model systems for various

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Table V. Molar Absorptivities of the 380-nm Band as a Function of Number of Oxo Ligands

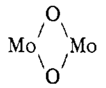
Complex	ϵ_{380}[a]	ϵ/(oxo ligand)
$Mo^{V}_2O_3(S_2CNEt_2)_4$[b]	5200	1730
$Mo^{VI}O_2(S_2CNEt_2)_2$[b,d]	3430 } 5160	1715
$Mo^{IV}O(S_2CNEt_2)_2$[b,d]	1730	1730
$Mo^{V}_2O_3[S_2C(1\text{-pip})]_4$[b]	5880	1960
$Mo^{VI}O_2[S_2C(1\text{-pip})]_2$[b,d]	4170 } 6120	2085
$Mo^{IV}O[S_2C(1\text{-pip})]_2$[b,c]	1950	1950
$Mo^{V}_2O_3[S_2C(4\text{-morph})]_4$[c]	5500	1830
$Mo^{VI}O_2[S_2C(4\text{-morph})]_2$[c,d]	3680 } 5210	1840
$Mo^{IV}O[S_2C(4\text{-morph})]_2$[c,d]	1600	1600

[a] Exact positions of peak maxima are listed in Table III. [b] In benzene solution. [c] In chloroform solution. [d] Preparation and properties to be reported.

enzymes,[1,6,16,28-43] the possible interrelationship of the molybdenum atoms in enzymes containing two such metal atoms per mole has received scant attention. Most model systems for nitrogenase have been based on the proposed mechanism that suggests that an "end-on" bound nitrogen molecule, bridging a molybdenum and an iron atom, is required for reduction.[44] A dimolybdenum active site, which interacts similarly with dinitrogen, has also been suggested.[38] Our interpretation[45] of enzymic nitrogen fixation is different from this and involves the "side-on" binding of a nitrogen molecule to a spin-paired molybdenum(IV) species with "carbenoid" properties which is responsible for all the enzymic chemistry. A closely related, intriguing problem concerns the nature of the relationship of the two molybdenum atoms in the various biological systems. Are they both active and working independently or do they operate in conjunction to produce the active species?

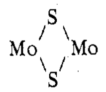
We have previously shown that oxobis(*N*,*N*-dialkyldithiocarbamato)molybdenum(IV) compounds can oxidatively add various unsaturated organic molecules.[6] The 1:1 adduct formed with diethyl azodicarboxylate hydrolyzes in solution to produce 1,2-bis(ethoxycarbonyl)hydrazine and the appropriate *cis*-dioxomolybdenum(VI). This latter compound is easily reduced to +IV state and is able to react again with the azo compound. We have previously suggested these reactions as a model for the interaction of dinitrogen with the nitrogenase active site.[6] This active molybdenum(IV) species is produced by the dissociation of the molybdenum(V) dimer in solution. Its presence was demonstrated by the addition of diethyl azodicarboxylate to a solution of a molybdenum(V) dimer when equimolar quantities of the appropriate *cis*-dioxomolybdenum(VI) and 1:1 diethyl azodicarboxylate-oxomolybdenum(IV) compounds were produced.

The chemistry described above suggests a possible mechanism of interaction by which the two molybdenum atoms in the various metalloproteins might produce the spin-paired molybdenum(IV) active species of nitrogenase. Two oxomolybdenum(VI) species in juxtaposition could produce a μ-dioxo-dimolybdenum(V) species



(similar to those described above) on reduction. Coordination of a suitable ligand (possibly a cysteine mercaptan group) to both molybdenum atoms could doubly protonate one of the bridging oxo ligands eliminating water while simultaneously producing the single-oxo-bridged system. This reaction would be analogous to the conversion of $Mo_2O_4(dtc)_2$ to $Mo_2O_3(dtc)_4$ in the presence of ligand. This dinuclear species may then dissociate *via* the equilibrium described above for the $Mo_2O_3(dtc)_4$ complexes to produce the active nitrogen-reducing molybdenum(IV) species and an inactive molybdenum(VI) species. After nitrogen binding and reduction is completed and ammonia is released by hydrolysis (which concomitantly produces a molybdenum(VI) species), the two molybdenum(VI) atoms could again interact *via* the oxo bridges and so continue the catalytic cycle. It may be that production of the active molybdenum(IV) species by this type of interaction is favored as it may occur with an electron donor of only moderate potential similar to those found in nature.

The oxidases may utilize such a system in reverse. In this case, the molybdenum(VI) species gives up its oxo ligand[6] and becomes reduced to molybdenum(IV) which then dissipates the electrons *via* similar bridging systems. If such a system indeed operates in molybdoenzymes, then our models indicate that oxo bridges are mandatory. We have found that the analogous μ-disulfido-dimolybdenum(V)



species do *not* react under similar conditions with excess ligand to produce a μ-sulfido bridge (Mo-S-Mo)[6] and therefore such systems cannot use this mechanism for the formation of the active spin-paired, "carbenoid" molybdenum(IV) species.

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Registry No. $Mo_2O_3(S_2CNMe_2)_4$, 20023-85-2; $Mo_2O_4(S_2CNMe_2)_2$, 50860-30-5; $Mo_2O_3(S_2CNEt_2)_4$, 20023-86-3; $Mo_2O_4(S_2CNEt_2)_2$, 50860-31-6; $Mo_2O_3[S_2C(1\text{-pip})]_4$, 20023-87-4; $Mo_2O_4[S_2C(1\text{-pip})]_2$, 50860-32-7; $Mo_2O_3[S_2C(4\text{-morph})]_4$, 50860-33-8; $Mo_2O_4[S_2C(4\text{-morph})]_2$, 50860-34-9; $Mo_2O_3[S_2CN(i\text{-Pr})_2]_4$, 50860-35-0; *cis*-$MoO_2(S_2CNMe_2)_2$, 39248-36-7; $MoO(S_2CNMe_2)_2(EtCN{=}NCO_2Et)$, 39584-76-4; $EtO_2CN{=}NCO_2Et$, 1972-28-7; $MoO[S_2C(1\text{-pip})]_2$, 50860-36-1; $MoO[S_2C(4\text{-morph})]_2$, 50860-37-2.

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